

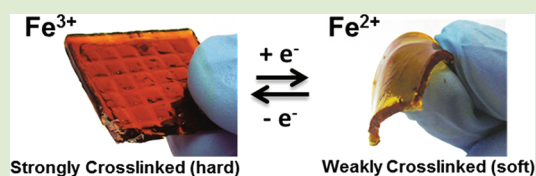
Manipulating Mechanical Properties with Electricity: Electroplastic Elastomer Hydrogels

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Supporting Information

ABSTRACT: The dawn of the 21st century has brought with it an increasing interest in emulating the adaptive finesse of natural systems by designing materials with on-demand, tunable properties. The creation of such responsive systems could be expected, based on historical precedent, to lead to completely new engineering design paradigms. Using a bioinspired approach of coupling multiple equilibria that operate on different length scales, a material whose bulk mechanical properties can be manipulated by electrical input has been developed. The new macroscale electroplastic elastomer hydrogels can be reversibly cycled through soft and hard states while maintaining a three-dimensional shape by sequential application of oxidative and reductive potentials. This input changes the cross-linking capacity of iron ions within the gel matrix, between a poorly coordinating +2 and a more strongly binding +3 oxidation state. Inclusion of carbon nanotubes in the hydrogel preparation increases conductivity and decreases transition time.



Nature integrates phenomena on multiple length scales and energy domains to establish extraordinary ranges of functionality. Among the numerous chemo-electro-mechanical examples are the rapid pressure and stiffness evolution observed in the motion of the Venus flytrap and neurological muscle control in animals.^{1,2} To create systems that exhibit responses in one domain or scale based on stimuli in another, Nature typically couples processes that transform the stimulus to a response through pathways or networks of mediating processes.^{3,4} We report the creation of a new material that uses electricity as a stimulus to produce, reversibly, a change in bulk-scale stiffness as a response (Figure 1). We term this new

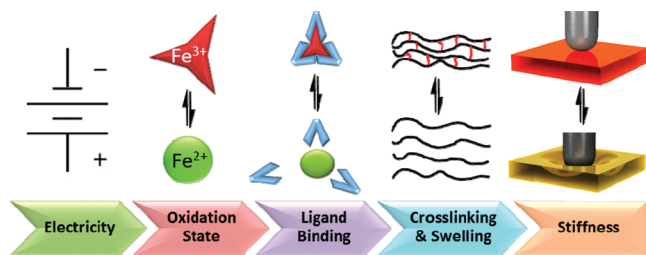


Figure 1. Electroplastic elastomer mechanism. Multistep pathway that reversibly converts electricity to a change in bulk stiffness in iron-crosslinked electroplastic elastomer hydrogels.

class of materials electroplastic elastomer hydrogels (EPEHs). Herein, we describe the synthesis, functional mechanism, and potential applications of this first generation material.

We chose to utilize the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple for developing these EPEHs because this system is both well-

behaved and well-understood; these two ions can be interconverted in a convenient potential window. As iron ions in different oxidation states have distinct coordination preferences, Fe^{3+} binds more strongly than Fe^{2+} to “hard” ligands, the change in oxidation state can be used to control the degree of cross-linking in a polymer bearing hard carboxylate side groups. Given the known correlation between cross-link density and the stiffness of polymeric materials, it follows that the mechanical properties of the bulk material should be reversibly controlled by the interconversion of Fe^{2+} and Fe^{3+} .

Although the creation of materials that respond to external stimuli is one of the most active frontiers of current materials development,^{5–11} EPEHs display a unique and valuable combination of properties not found in any other system: (1) reversible changes in mechanical stiffness using only electrical input and (2) 3D-macroscale dimensions in all states. The mechanism that underlies the change in bulk mechanical properties of EPEHs, forming and breaking polymer chain cross-links, has been exploited by others. However, few of these materials are reversible and of those that are, all have stimulus-defined limitations not shared by EPEHs. For example, many systems are not self-contained; they require manual addition and removal of solvents or chemicals for each response.^{12,13} Other systems are stimulated by temperature^{14,15} which, unlike electricity, is difficult to direct to a specific location in the material. Moreover, the required activation temperatures could prove impractical to access and implement for specific

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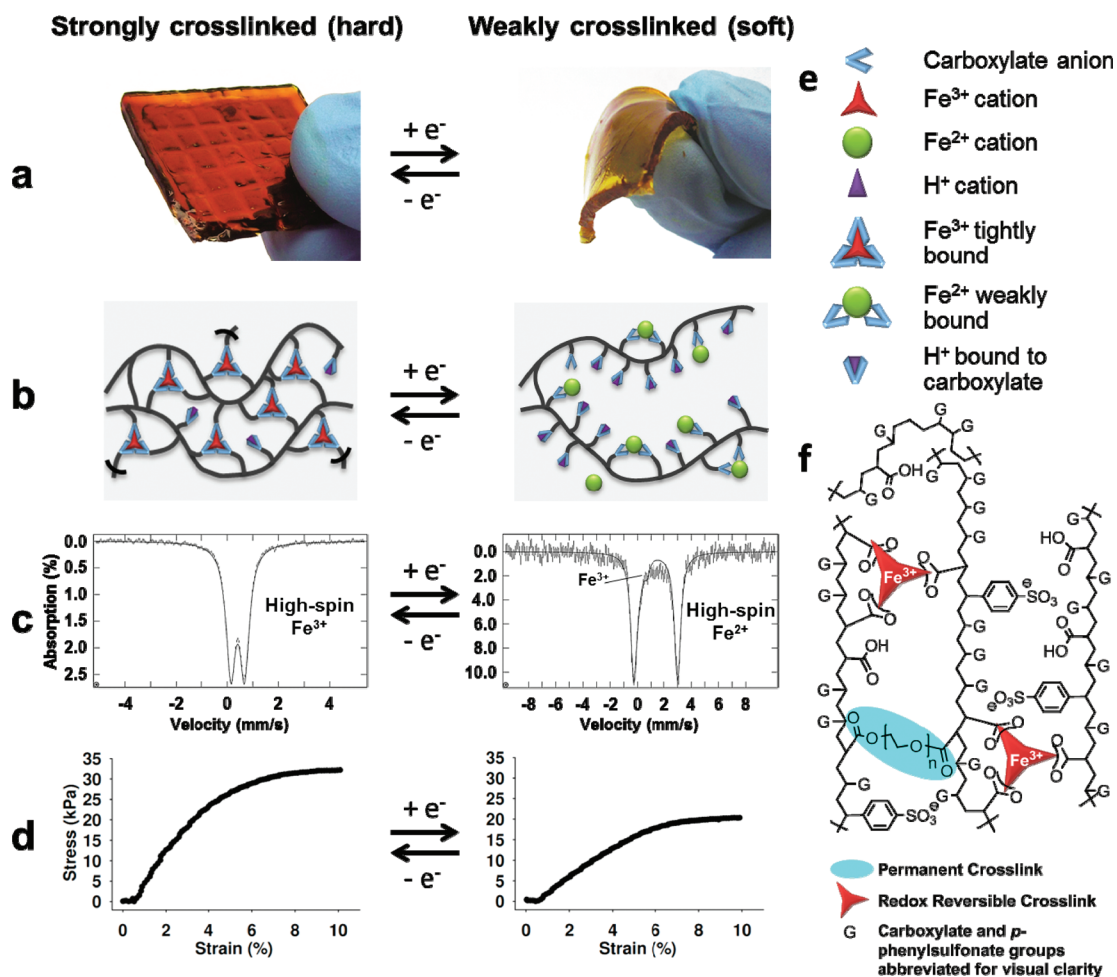


Figure 2. Redox-mediated switching between hard and soft states for iron-based electroplastic elastomer. Reversible electrochemical conversion of stiff Fe^{3+} -cross-linked hydrogel (left) to softer Fe^{2+} hydrogel (right). (a) Hydrogel in oxidized (left) and reduced (right) states held in gloved hand. (b) Cartoons depicting differences in intra- and interchain cross-linking for Fe^{3+} and Fe^{2+} . (c) Mössbauer spectra of hydrogel samples in the oxidized and reduced states. (d) Mechanical stress/strain curves for EPEHs in the oxidized and reduced states under compression. (e) Key for b. (f) Representation of the chemical structure of the hydrogel in the oxidized state.

applications. A need exists for materials whose properties can be adjusted on-demand without requiring a change in the overall environment of the material. Electricity, which is employed as the stimulus for EPEHs, satisfies these requirements and offers practical advantages including ease of access, portability, and a sophisticated technology infrastructure.

The second key property of the EPEHs, one not shared by other electrically reversible systems, is the maintenance of a three-dimensional shape in all states. Electrically stimulated polymeric materials that exhibit mechanical property changes other than osmotically controlled mechanical actuation^{16–18} are generally stimulated either as cast films (not macroscopic in all dimensions)^{7,19} or they undergo a transformation between sol and gel states (shape is neither controlled nor maintained).^{20–27} Tong and co-workers, for example, demonstrated that using either electrochemistry or light the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple can be used to induce a sol–gel transition in poly(acrylic acid).^{21,23} EPEHs, in contrast, have macroscopic dimensions in all directions and maintain a nonzero stiffness in all states, which enables shape to be retained while compliance is tuned.

EPEH samples were prepared by simple free-radical copolymerization of commercially purchased monomers

under standard conditions. Sodium acrylate, sodium (4-styrene sulfonate), and polyethylene glycol diacrylate (PEG-DA, $M_n = 575$) in a weight ratio of 12:8:1 were reacted in aqueous solution with an ammonium persulfate catalyst at 85 °C for 1.5 h to give a soft, colorless hydrogel. The presence of the permanent PEG-DA cross-links gives the hydrogels a baseline shape defined by the reaction vessel. Cation exchange of sodium ions for Fe^{2+} or Fe^{3+} was accomplished by submersion of the hydrogel in a solution of 2.0 M FeCl_2 or FeCl_3 and 0.5 M citric acid for a period of 20–48 h. Exchange with Fe^{2+} produced samples that were pale yellow-green in color and slightly smaller than the original hydrogel, due to coordinative cross-linking (Figure S1). Samples prepared with Fe^{3+} were orange-red and even more contracted in dimension, up to 50% smaller in thickness than the predoped samples (Figure 2f, Figure S1). Hydrogels were transparent and appeared homogeneous throughout. Although the standard samples prepared for this article are relatively small, $2.5 \times 2.5 \times 0.2$ cm after doping with Fe^{3+} , the procedure is inherently scalable to nearly any sample size.

Samples prepared independently with comparable Fe^{2+} and Fe^{3+} ion contents (Table S1, ca. 1.2 mmol/cm³) exhibited more than an order of magnitude difference in modulus when

subjected to mechanical testing using an indentation methodology. Compressive moduli of 0.06 and 2.1 MPa were measured for Fe^{2+} and Fe^{3+} samples that were prepared, measured, and analyzed for iron content using identical protocols. Moduli higher than 2.1 MPa can be achieved for Fe^{3+} samples by adjustments in doping conditions.

The mechanical properties of the EPEH samples are controlled by the electrolytic interconversion of the Fe^{3+} and Fe^{2+} within the same bulk sample. An EPEH sample of standard dimensions was prepared directly on a glassy carbon electrode (Figure S2). After in situ Fe^{3+} exchange, the sample was protected from exposure to light and subjected to a reducing potential of -0.8 V for 18 h in an electrolyte solution of 0.5 M citric acid and 2.0 M FeCl_2 . Prior to each electrolysis experiment, the electrolyte solution was purged with N_2 to remove dissolved oxygen and an N_2 atmosphere was maintained for the duration. After reduction, the sample became softer to the touch, pale orange-yellow in color, and was visibly swollen relative to the initial state (Figure 2a, right). Exchange of the tightly bound Fe^{3+} with the Fe^{2+} present in the electrolyte solution (necessary for the reduction step in samples that will be cycled between states, vide infra) is not significant; a control submerged for the same period in the same solution without electrolysis did not soften nor change color. It is important to note that the reduction occurs analogously when the electrolyte solution comprises only KNO_3 (0.2 M, pH 1). Also, leaching of hydrogel-bound Fe^{3+} into the electrolyte solution is negligible under these conditions. Mössbauer analysis of both the starting sample and the sample produced by reduction established unambiguously that a nearly complete conversion of the high-spin Fe^{3+} in the sample to high-spin Fe^{2+} occurred (Figure 2c). Air oxidation during Mössbauer sample preparation and/or incomplete reduction is responsible for the small Fe^{3+} shoulder (<15%). The sample color for the reduced EPEH, which is orange-yellow rather than the yellow-green that is characteristic of freshly prepared Fe^{2+} -doped hydrogels, is likewise consistent with the presence of a small fraction of the more intensely colored Fe^{3+} cross-links.

Oxidation of a freshly prepared Fe^{2+} EPEH in 2 M FeCl_2 , 0.5 M citric acid produced the opposite changes in color and mechanical properties. After oxidation at 1.2 V for a period of 14 h (light excluded, N_2 atmosphere), the sample became darker orange in color, thinner, and stiffer (Figure 2a, left; grid pattern caused by macroporous pressure cap). The presence of FeCl_2 in the electrolyte facilitates the oxidation step because, as per the design of the system, Fe^{2+} is weakly bound and will, therefore, rapidly equilibrate with the external solution. Figure 2d shows stress–strain curves that were acquired by indentation testing of electrode-mounted samples after oxidation (left) and reduction (right). Chemical oxidation of Fe^{2+} samples by treatment with ammonium persulfate gave analogous physical and optical changes. EPEHs with Fe^{2+} cross-links also slowly oxidize in air over the course of hours to days, as shown by changes in color and stiffness of samples stored in humid environments to prevent drying.

The oxidation/reduction is reversible, as can be seen in Figure 3a. The compressive moduli for a single EPEH sample that was subjected to two cycles of reduction and oxidation switch reversibly between about 1.0 and 0.6 MPa. At each stage, the samples displayed the color profile and degree of swelling that is characteristic of the particular oxidation state. Although the changes are reproducible and the moduli are clearly distinct, the difference in modulus range is smaller than that observed

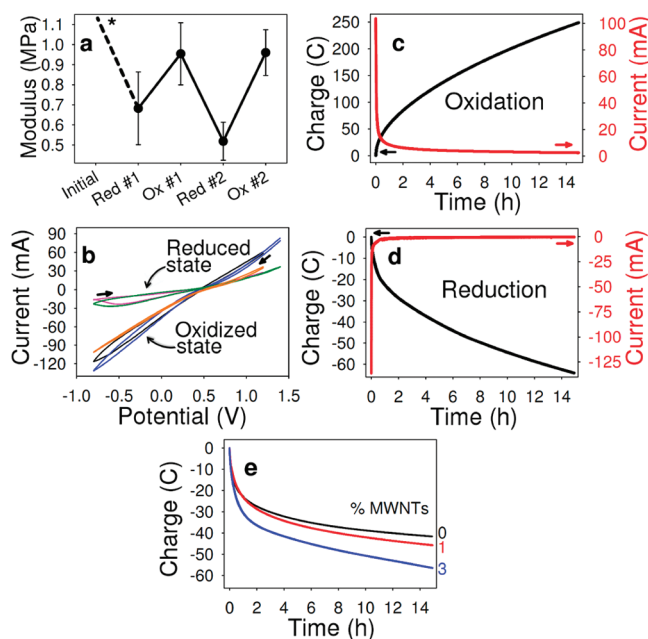


Figure 3. Mechanical and electrochemical characterization of redox-switched electroplastic elastomers. (a) Compressive moduli for oxidized and reduced samples. *Est. > 2 MPa. (b) Cyclic voltammograms before and after redox cycles. (c, d) Typical chronoamperometry and chronocoulometry for redox transitions. (e) Reduction of carbon-nanotube modified electroplastic elastomers. Improved charge transport for EPEH samples prepared with 0–3% by weight carbon nanotubes (MWNTs).

for samples directly prepared from Fe^{2+} and Fe^{3+} . We attribute the differences to a combination of two factors: (1) iron equilibration between the sample and the electrolyte under experimental conditions and (2) air oxidation of reduced samples during sample transport and mechanical measurement.

Figure 3b–d shows the electrochemical characteristics of the hydrogels used for these proof of concept experiments. In Figure 3b, the cyclic voltammograms (CVs) acquired at each stable state represented in Figure 3a are plotted. The overlay demonstrates that the oxidized and reduced states are distinct and reproducible under cycling conditions. Example chronoamperometry and chronocoulometry plots (Figure 3c and d, see Supporting Figures S3–S6 for compilation of all data) establish that the redox process is slower than desired for applications. It should be noted that the total charge passed is much greater for the oxidation process because of the presence in the electrolyte solution of excess Fe^{2+} , which is maintained in constant excess within the system, not added or removed, for both the oxidation and the reduction cycles.

Although the EPEHs are new materials and have not been optimized, they already manifest a combination of features that suggest that they have an exceptional potential for further development and applications: scalability, reversibility, stability, tunability, and effective delivery of the stimulus. *Scalability is a key characteristic of the EPEH materials.* Many intriguing nano- and subnanoscale phenomena have not successfully been translated into macroscale responses. By employing Nature's tactic of using multiple mediating steps it has been possible to translate an atomic scale phenomenon, metal-ion redox transformation, to a mechanical response that is readily observable on a macroscale. The coupling of the mediating steps was a nontrivial challenge, however, as it was necessary to

create conditions in which all the relevant equilibria could operate in their functional regions. pH, for example, must be reasonably low to prevent the formation of insoluble metal oxidation products but maintained above the minimum threshold required for iron ions to compete effectively with protons for the carboxylate groups. Citrate ion, which facilitates iron mobility, is another necessary component of the system whose concentration must be strictly controlled because it assists some steps and hinders others. EPEHs are also physically scalable. The hydrogels are prepared from nonexotic reagents and the same basic procedure is applicable to samples on larger scales; we have prepared samples with thicknesses up to 2.5 cm and length \times width dimensions >100 cm².

Reversibility and stability of the different states are also important features of the EPEHs. The redox process cycles the metals between two states that are stable as long as the material is protected from environmental oxidants and reductants. The electrical power used to switch states is not necessary to maintain them. There is also no theoretical limit on the number of times that the electrochemical process can be repeated. It should be noted that the aqueous Fe²⁺ reservoir is an essential component because the uptake and exclusion of water and ions in the hydrogel is integral to the manifestation of oxidation-state-dependent mechanical properties.

EPEHs are highly tunable both in their preparation and in their implementation. By varying the percentage of carboxylate monomers or PEG-DA cross-linking agent relative to the other components, the fundamental stiffness can be adjusted within the limits of maintaining sample integrity and hindering ion migration. There is also the potential to adjust the stiffness through a full continuum of values within its range by partial redox.

The final characteristic of the system, delivery of stimulus, is still evolving. Although we have demonstrated that iron ions can be reduced and oxidized throughout the sample in the EPEH hydrogels, the process is slow because the electrode is localized on one face. The chronocoulometry data (Figures S3–S6) and direct observation suggest that the transformation is largely diffusion controlled (with possible contributions by electron exchange).²⁸ In a preliminary experiment, the effect of increasing the conductivity of the hydrogel on conversion time was probed. EPEH samples prepared with the addition of 1–3% vinyl-functionalized multiwalled carbon nanotubes (MWNTs) were doped with Fe³⁺ and then subjected to reducing conditions. The charge versus time response changed dramatically, as shown in Figure 3e. The time to pass 40 Coulombs decreased from 11.9 h for hydrogel with no nanotubes to 3.2 h for 3% MWNTs. Although the ratio of charge consumed by reduction of the nanotubes versus Fe³⁺ under these conditions has not been determined, qualitative examination of the hydrogel color and behavior is consistent with a significant decrease in time for iron reduction. We hypothesize that the nanotubes improve conduction such that the distance that iron atoms must diffuse for reduction is decreased. These data are encouraging and suggest that conversions on the time-scale of minutes would be accessible with further refinements.

Throughout the history of design, the materials available to engineers have been predominantly fixed in their properties, with some exceptions as mentioned above. EPEHs represent the first of a novel class of materials that act in a self-contained system to change mechanical properties with electrical stimulus. The availability of materials of this type will potentially spawn

new design paradigms that in turn lead to innovations in aerospace, manufacturing, consumer products, robotics, etc.

■ EXPERIMENTAL METHODS

Typical hydrogel preparation: Sodium acrylate (4.8 g, 51 mmol) and sodium(4-styrene sulfonate) (3.2 g, 14.3 mmol) were combined with 36 mL of deionized water and gently heated (<40 °C) until all solids were dissolved. Poly(ethylene glycol) diacrylate (PEG-DA, $M_n = 575$, 400 μ L, 0.78 mmol) was added and the mixture was purged with N₂ for 5 min. Ammonium persulfate (APS, 72 mg, 0.47 mol %) was added as a radical initiator for copolymerization. Note: adjustments in PEG-DA stoichiometry relative to the other monomers produced hydrogels that were qualitatively stiffer (increased PEG-DA) or softer (decreased PEG-DA).

Depending on the dimensions of the sample being prepared, 2–8 mL of the reaction mixture was pipetted into a mold. For electrochemical experiments the mold for the sample was created by temporarily affixing, using PDMS adhesive, a square glass cell to a Teflon base bearing a freshly polished glassy carbon electrode (GCE). The mold/sample combination was then heated at 85 °C for 1.5 h. After cooling to RT, the hydrogel was doped by simple submersion in either a solution of 2.0 M FeCl₂/0.5 M citric acid or 2.0 M FeCl₃/0.5 M citric acid for a period of 20–48 h (Figure S1). A 1:3 ratio by volume of doping solution to prepolymer was used.

Vinyl-functionalized MWNTs were synthesized as reported in the literature²⁹ from commercially purchased COOH-MWNTs. Prior to hydrogel polymerization MWNTs were suspended in DI water and dispersed in an ultrasonic water bath for 30 min. The dispersed MWNTs were then added to the dissolved monomers (mixed in the same ratio as for simple hydrogels) and APS was added as a radical initiator. Polymerization and iron doping was performed as described above.

Electrochemical measurements: Cyclic voltammetry (CV) and amperometry measurements were carried out with a CH Instruments Electrochemical workstation Model 430A (Austin, TX) at RT using a three-electrode system composed of a glassy carbon plate (GCE, 25 \times 25 mm) working electrode, a Ag/AgCl reference electrode, and a platinum grid counter electrode (Figure S2). The GCE was polished with 0.3 μ m Al₂O₃ paste and cleaned thoroughly in an ultrasonic water bath for 5 min prior to each use. The CV and amperometry experiments for reduction and oxidation were carried out in 15 mL of 2.0 M FeCl₂/0.25 M citric acid, pH \sim 1.8. CV data were acquired at a scan rate of 100 mV/s over a voltage range of 1.2 to -0.8 V. Bulk electrolysis was performed in the same electrolyte solution for up to 40 h (reduction potential -0.8 V, oxidation potential $+1.2$ V). All electrochemical experiments were performed under N₂ atmosphere with careful exclusion of ambient light to prevent the photoreduction of Fe³⁺ ions in the presence of citric acid.²³

■ ASSOCIATED CONTENT

Supporting Information

Materials and methods, photos of Fe²⁺ and Fe³⁺ hydrogels, Mössbauer spectroscopy, mechanical and electrochemical measurements with cell schematic and photo of cell, chronoamperometry and chronocoulometry plots for redox cycling of Fe³⁺ hydrogel, quantification of iron and calibration curve, and mechanical properties of Fe²⁺ and Fe³⁺ hydrogels. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

T.Y.M. conceived the idea, designed experiments, analyzed results, and wrote the manuscript; W.W.C. conceived the idea, developed applications, and analyzed results; D.H.W. and

L.M.W. designed experiments and analyzed results; P.C.-M., M.P.D., T.P., and N.M.P. designed and carried out experiments; J.T.A. designed and carried out experiments and organized data/figures for publication.

Notes

The authors declare no competing financial interest.

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